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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(54) Title: PROCESS FOR THE PREPARATION OF STYRENES

(57) Abstract

Process for the preparation of styrene or substituted styrenes comprising the gas phase dehydration of 1–phenyl ethanol or substituted 1–phenyl ethanol in the presence of a solid acidic catalyst comprising a zeolite and a binder material, wherein the weight ratio of zeolite to binder is in the range of from 1:99 to 90:10 and wherein the following relation applies: $0 < K < 5$ with: $K = V/S * [(Pz * fz) + (Pb * fb)]^{1/2}$, wherein: V/S is the volume/surface ratio of the catalyst used in mm; fz is the weight fraction of zeolite present in the catalyst in grams zeolite per gram catalyst; fb is the weight fraction of binder present in the catalyst in grams binder per gram catalyst; Pz is the intrinsic productivity of zeolite expressed as grams styrene produced per gram of the zeolite per hour, as measured for pure zeolite samples of small particle size (i.e. < 0.1mm) at the temperature applied in gas phase dehydration and at a conversion of 1–phenyl ethanol into styrene below 80 %; and Pb is the intrinsic productivity of the binder expressed as grams styrene produced per gram of binder per hour, as measured for pure binder samples of small particle size (i.e. < 0.1mm) under the same conditions as used for determining Pz.

PROCESS FOR THE PREPARATION OF STYRENES

The present invention relates to a process for the preparation of styrene or substituted styrenes, more specifically to such a process comprising the gas phase dehydration of 1-phenyl ethanol or substituted 1-phenyl ethanols.

Within the further context of the present application the term "substituted styrenes" refers to vinyl aromatic compounds of the general formula

$$Ar-CR=CH_2,$$
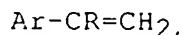
wherein Ar is a phenyl, tolyl or xylyl group and R is H or a methyl group. When referring to "styrene" in the present application, these substituted styrenes are also included, unless indicated otherwise. Similarly, the term "substituted 1-phenyl ethanols" refers to aromatic alcohols of the general formula

$$Ar-C(R)(CH_3)-OH$$
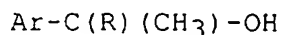
wherein Ar and R are as defined above. When referring to "1-phenyl ethanol", these substituted 1-phenyl ethanols are also included, unless indicated otherwise.

A commonly known method for manufacturing styrene is the coproduction of propylene oxide and styrene starting from ethylbenzene (a Styrene Monomer/Propylene Oxide or SM/PO process). In general such process involves the steps of (i) reacting ethylbenzene with oxygen or air to form ethylbenzene hydroperoxide, (ii) reacting the ethylbenzene hydroperoxide thus obtained with propene in the presence of an epoxidation catalyst to yield propylene oxide and 1-phenyl ethanol, and (iii) converting the 1-phenyl ethanol into styrene by dehydration using a suitable dehydration catalyst. The present invention particularly focuses on the last

step, i.e. the dehydration of 1-phenyl ethanol to yield
styrene.

Step (iii) of the process described above, i.e. the
production of styrene by dehydrating 1-phenyl ethanol,

5   can be carried out in different ways as is well known
in the art. In general, the dehydration can be carried
out in the gas phase or in the liquid phase in the
presence of a dehydration catalyst. Suitable
dehydration catalysts are known and include for

10   instance acidic materials like alumina, alkali alumina,
aluminium silicates and H-type synthetic zeolites.
Dehydration conditions are also well known and usually
include reaction temperatures of 50-205 °C, typically
100-200 °C, for liquid phase dehydration and

15   210-320 °C, typically 280-310 °C, for gas phase
dehydration. Pressures usually range from 0.1 to
10 bar.

In GB-A-2,176,801 the liquid-phase dehydration of
an aromatic alcohol into an aromatic vinyl compound is

20   described, wherein the dehydration is carried out at
elevated temperature in the presence of a solid acid
catalyst. Aluminium silicate and H-type synthetic
zeolites are mentioned as suitable catalysts, but no
further details as to the properties of these materials

25   is given.

In Takahashi et al., The Canadian Journal of
Chemical Engineering, Vol. 66, June 1988, pp. 433-437,
a process for the liquid phase dehydration of 1-phenyl
ethanol into styrene is described using various types

30   of acidic catalysts. The catalysts used include silica-
alumina, Y type zeolites, mordenites, H-ZSM-5 and
several aluminas, all used in the form of crushed
particles of 24-32 mesh (corresponding with 0.5 to
0.7 mm). This publication concludes that when the

35   concentration of effective acid sites on the catalyst

increases, the dehydration reaction rate increases, but the styrene selectivity decreases. A certain alumina catalyst was found to provide the best balance between reaction rate and styrene selectivity.

In JP-A-61/72727 the gas-phase dehydration of 1-phenyl ethanol into styrene is described, wherein a zeolite is used as the dehydration catalyst. The patent application does not give any further details as to the types and properties of suitable zeolites, except that in the working examples OSZ-250, a H-Y-type zeolite, is used in the form of crushed particles having a size of 32-60 mesh (corresponding with 0.25-0.50 mm). In the working example the feed solely consisted of 1-phenyl ethanol without other compounds being present.

The present invention aims to provide an effective dehydration process for converting 1-phenyl ethanol into styrene, which process can also be used in the dehydration step of a commercial SM/PO process. In such a process the feed to the dehydration section will not only contain 1-phenyl ethanol, but also substantial amounts of other compounds formed in the preceding sections. Examples of such compounds are 2-phenyl ethanol, methyl phenyl ketone, some styrene monomer, ethylbenzene and water.

It has been found that 1-phenyl ethanol either as such or in a process stream in an SM/PO process can be very effectively converted into styrene in a gas phase dehydration process by selecting a zeolitic catalyst meeting certain specific requirements.

Accordingly, the present invention relates to a process for the preparation of styrene or substituted styrenes comprising the gas phase dehydration of 1-phenyl ethanol or substituted 1-phenyl ethanol in the presence of a solid acidic catalyst comprising a zeolite and a binder material, wherein weight ratio of

zeolite to binder is in the range of from 1:99 to 90:10
and wherein the following relation applies:

$$0 < K < 5 \tag{1}$$

with:

5
$$K = V/S * [(Pz * fz) + (Pb * fb)]^{\frac{1}{2}} \tag{2}$$

wherein:

V/S is the volume/surface ratio of the catalyst used in
mm;

fz is the weight fraction of zeolite present in the

10   catalyst in grams zeolite per gram catalyst;

fb is the weight fraction of binder present in the
catalyst in grams binder per gram catalyst;

Pz is the intrinsic productivity of the zeolite
expressed as grams styrene produced per gram of zeolite

15   per hour, as measured for pure zeolite samples of small
particle size (i.e. < 0.1 mm) at the temperature
applied in gas phase dehydration and at a conversion of
1-phenyl ethanol into styrene below 80%; and

Pb is the intrinsic productivity of the binder

20   expressed as grams styrene produced per gram of binder
per hour, as measured for pure binder samples of small
particle size (i.e. < 0.1 mm) under the same conditions
as used for determining Pz.

The catalyst to be used comprises zeolite and

25   binder in a weight ratio of zeolite to binder of from
1:99 to 90:10, preferably of from 3:97 to 35:65.
Suitable binder materials include inorganic oxides like
silica, alumina, boria, zirconia, titania and silica-
alumina as well as organic materials like carbon or

30   polymers. Of these, the substantially inert binder
materials silica and alumina are preferred. The zeolite
to be used in principle may be any zeolite having
sufficient acidity to catalyse the dehydration of
1-phenyl ethanol. Suitable zeolites, then, include

35   H-ZSM-5, H-ZSM-23, H-mordenite, H-Y-zeolite and beta-

zeolite, but also silica-alumina phosphate molecular
sieve materials, such as SAPO-34. However, other acidic
zeolitic materials may be applied as well.

The catalyst to be used must meet very specific
requirements as regards particle size, outer surface
and zeolite content. These requirements are summarised
in equations (1) and (2):

$$0 < K < 5 \tag{1}$$

with:

$$K = V/S * [(Pz * fz)+(Pb * fb)]^{\frac{1}{2}} \tag{2}$$

wherein V/S, Pz, Pb, fz and fb have the meaning as
indicated above. The quotient of volume V (in mm^3) and
outer surface S (in mm^2) is expressed in mm and is a
measure for the particle size and its shape. For
spherical catalyst particles, V/S is 1/6 of the
particle diameter. For cylindrical catalyst particles
V/S is 1/4 of the particle diameter. For catalyst
particles shaped as trilobes, stars, quadrulobes,
wokkels and the like, the ratio V/S will be smaller
than 1/4 of the outer diameter of the enclosing
cylinder. It has been found advantageous to select V/S,
Pz, Pb, fz and fb such that K has a value of less than
2, preferably of less than 0.5 and most preferably of
less than 0.2.

The weight fractions of zeolite (fz) and binder
(fb) indicate the amounts of zeolite and binder in
grams per gram of catalyst. The sum of fz and fb is
equal to 1, i.e. the catalyst consists of zeolite and
binder. The productivities Pz and Pb in fact indicate
the dehydration activity of the pure zeolite and pure
binder, respectively. For the purpose of the present
invention it is preferred that the binder is
substantially inert, so that Pb = 0. As a result, the
following relation applies:

$$K = V/S * (Pz * fz)^{\frac{1}{2}} \qquad (3)$$

The conditions under which the dehydration is carried
out may vary within wide limits, but should anyhow be
such that the 1-phenyl ethanol is in the gas phase. At

5   atmospheric pressure this implies that the reaction
temperature should be higher than the boiling
temperature of 1-phenyl ethanol, which is 203-204 °C.
At subatmospheric conditions, however, the reaction
temperature may be lower. In general, the gas phase

10   dehydration is suitably carried out at a temperature in
the range of from 205 to 300 °C, preferably 210 to
250 °C, at a pressure of from 0.5 to 5 bar.

The process according to the present invention can
be carried out in different operational modes in terms

15   of the way in which the catalyst is used. In one
embodiment of the present invention the catalyst is
used in the form of particles having an average
particle size of at least 0.5 mm, preferably from 1 to
10 mm, more preferably from 1.5 to 5 mm, in a packed

20   fixed bed. Such relatively large particle sizes are
preferred to keep the pressure drop within the reactor
at an acceptable level. In this mode of operation the
catalyst particles are randomly packed into a bed over
which the feed comprising 1-phenyl ethanol is passed

25   upwardly or downwardly. The catalyst particles may have
any desired shape including spherical, (hollow)
cylindrical, trilobe, star-shaped, pellet-shaped etc.
In another embodiment of the present invention the
catalyst is used in the form of particles having an

30   average particle size of 0.5 mm or less, preferably
from 0.02 to 0.1 mm, in a fluidised bed. In this mode
of operation spherical catalyst particles are normally
applied, so that the ratio V/S equals 1/6 of the
diameter of the catalyst particles. Since the catalyst

35   particles are free flowing and hence are exposed to

relatively severe mechanical forces, a certain minimum
amount of binder material should be present to give the
catalyst particles sufficient strength. Preferred
binder contents are 20% by weight or more, more
preferably at least 30% by weight. The gaseous feed
enters the fluidised bed reactor at the bottom at a
certain velocity, thus helping to keep the catalyst bed
in its fluidised state, and the styrene-containing
product leaves the reactor at the top.

In a still further embodiment of the present
invention the catalyst is applied as a layered
catalyst, which is as a thin layer on either small
support particles or on a monolithic support or a
structured packing. In these forms the catalyst is most
suitably applied in a fixed bed operation. The coated
catalyst particles, however, could also be applied in a
fluidised bed operation, if the particles are
sufficiently small (i.e. < 100 µm). In general,
monolithic catalysts are continuous, unitary structures
containing many narrow, parallel straight or zigzag
passages. Catalytically active ingredients are
distributed uniformly in a porous layer deposited on
the walls of the channels in the monolithic structure.
A frequently applied monolithic structure is the
honeycomb structure. The essence of monolithic
catalysts is the very thin layers, in which internal
diffusion resistance is small. A structured packing is
an open cross-flow structure, which can serve as a
catalyst carrier by applying a thin layer of
catalytically active material on the walls of the
channels. Such structured packings are for instance
available from Sulzer Chemtech. An example of a
structured packing is a foam containing channels. For
all layered catalysts (coated particles, monolithic
supports and structured packings) the thickness of the

applied catalyst layer will usually vary between 1 and 100 μm, more suitably 1 and 50 μm. The V/S ratio in this case will be about equal to the layer thickness assuming that the half of the total surface bound to the support is not accessible for the reactant gas.

The invention is further illustrated by the following example without restricting the scope of the invention to the particular embodiments illustrated in this example.

Example

The experiments were carried out in a stainless steel reactor (13 mm internal diameter; 30 cm length) equipped with an internal thermowell (0.5 outer diameter). The feed was passed downwardly through the reactor. The catalyst particles used were diluted with glass beads (2 mm diameter) prior to filling the central segment of the reactor. The feed line was traced to the reactor temperature to allow the feed to vaporise. The product was collected and analysed by means of gas chromatography.

The feed consisted of:

    82% by weight of 1-phenyl ethanol
     5% by weight 2-phenyl ethanol
    11% by weight methyl phenyl ketone
    1-2% by weight of water and
    the balance up to 100% by weight of styrene plus ethyl benzene.

The catalyst used was based on H-ZSM-5 zeolite, which was extruded with SiO_2 into trilobes of 1.6 mm outer diameter. Two batches were prepared: one with 20% by weight zeolite and one with 80% by weight zeolite. The extruded catalyst was also tested in the form of crushed particles of about 0.2 mm.

The reactor was loaded with a sufficient amount of catalyst to have about 0.5 grams of zeolite in the

reactor. The catalyst was heated under a flow of
nitrogen, initially rapidly up to 80 °C, then within
2 hours to 120 °C and subsequently rapidly up to the
reaction temperature of 220 °C, at which temperature
the catalyst was kept for 2 hours. Then, the feed was
introduced into the reactor and the catalyst was
contacted with the vaporised feed at a rate of 18 g/h
(corresponding with a weight hourly space velocity of
30 grams 1-phenyl ethanol per gram zeolite per hour)
and atmospheric pressure for several days.

The productivity P_z of the zeolite was determined
by running the pure zeolite powder diluted in glass
beads at 220 °C and at a 1-phenyl ethanol conversion of
approximately 55%. The P_z had a value of 5 g styrene/g
zeolite/h.

The results are indicated in Table I. The
abbreviations D, Conv. and Sel. refer to catalyst
particle diameter, conversion and selectivity,
respectively. The conversion is calculated on the basis
of the carbon content C of the feed and of the
unconverted feed leaving the reactor:

$$\text{Conversion} = \frac{C(\text{feed}) - C(\text{unconverted feed})}{C(\text{feed})} \times 100\%$$

The carbon content of the unconverted feed is the
difference between the total carbon content of the
product stream that leaves the reactor and the C of the
styrene formed.
The selectivity is calculated on the basis of the
carbon content of the styrene formed and the carbon
content of the feed:

$$\text{Selectivity} = \frac{C(\text{styrene})}{C(\text{feed})} \times 100\%$$

TABLE I   Results

Run No.	D (mm)	fz (g/g)	V/S (mm)	K	Time (h)	Conv. (%)	Sel. (%)
1	0.2	0.2	0.033	0.03	5	95	98
					50	92	97
					100	90	98
2	0.2	0.6	0.033	0.05	5	95	90
					50	85	93
					100	81	92
3	1.6	0.2	0.400	0.38	5	95	95
					50	80	94
					100	65	92
4	1.6	0.6	0.400	0.66	5	60	75
					50	52	80
					100	45	82

From Table I it can be seen that the selectivity is high and stable for catalysts having a K of less than 0.5 (runs Nos. 1-3). The catalyst with a K of more than 0.5 is still performing adequately, but shows a somewhat lower selectivity which is also less stable. The conversion for the catalysts used in runs Nos. 1-3 is also somewhat higher than the conversion for the catalyst used in run No. 4, although the latter is still sufficiently high.

Comparative Example

Run No. 3 was repeated, but with a liquid in stead of a vaporous feed. Two runs of 48 hours each were carried out, one at 120 °C (run No. 5) and one at 170 °C (run No. 6), at a space velocity of 10 g 1-phenyl ethanol/g zeolite/h.

It was found that in both runs the conversion was higher than 80%, but the selectivity did not exceed 30% (run No. 5) and 50% (run No. 6).

Hence, the comparative examples demonstrate that
the process according to the present invention must be
a gas phase process.

C L A I M S

1. Process for the preparation of styrene or
substituted styrenes comprising the gas phase
dehydration of 1-phenyl ethanol or substituted 1-phenyl
ethanol in the presence of a solid acidic catalyst
comprising a zeolite and a binder material, wherein the
weight ratio of zeolite to binder is in the range of
from 1:99 to 90:10 and wherein the following relation
applies:

$$0 < K < 5 \qquad\qquad\qquad (1)$$

with:

$$K = V/S * [(Pz * fz)+(Pb * fb)]^{\frac{1}{2}} \qquad (2)$$

wherein:

V/S is the volume/surface ratio of the catalyst used in
mm;

fz is the weight fraction of zeolite present in the
catalyst in grams zeolite per gram catalyst;

fb is the weight fraction of binder present in the
catalyst in grams binder per gram catalyst;

Pz is the intrinsic productivity of the zeolite
expressed as grams styrene produced per gram of zeolite
per hour, as measured for pure zeolite samples of small
particle size (i.e. < 0.1 mm) at the temperature
applied in gas phase dehydration and at a conversion of
1-phenyl ethanol into styrene below 80%; and

Pb is the intrinsic productivity of the binder
expressed as grams styrene produced per gram of binder
per hour, as measured for pure binder samples of small
particle size (i.e. < 0.1 mm) under the same conditions
as used for determining Pz.

2. Process according to claim 1, wherein K has a value
of less than 2, preferably of less than 0.5.

3. Process according to claim 1 or 2, wherein the intrinsic productivity of the binder, Pb, is essentially zero, so that:

$$K = V/S * (Pz * fz) \qquad (3)$$

wherein V/S, Pz and fz are as defined in claim 1.

4. Process according to any one of the preceding claims, wherein the weight ratio of zeolite to binder is in the range of from 3:97 to 35:65.

5. Process according to any one of the preceding claims, wherein the binder is silica or alumina.

6. Process according to any one of the preceding claims, wherein the temperature at which the gas phase dehydration is carried out is in the range of from 205 to 300 °C, preferably 210 to 250 °C, at a pressure of from 0.5 to 5 bar.

7. Process according to any one of the preceding claims, wherein the zeolite is H-ZSM-5, H-ZSM-23, H-mordenite, H-Y-zeolite, beta-zeolite or a silica-alumina phosphate, such as SAPO-34.

8. Process according to any one of the preceding claims, wherein the catalyst is used in the form of particles having an average particle size of at least 0.5 mm in a packed fixed bed.

9. Process according to any one of claims 1-7, wherein the catalyst is used in the form of particles having an average particle size of 0.5 mm or less and in a fluidised bed.

10. Process according to any one of claims 1-7, wherein the catalyst is applied as a coating on a monolithic support or a structured packing in a fixed bed operation.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C07C15/44   C07C1/24   B01J29/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8345 Derwent Publications Ltd., London, GB; Class A41, AN 83-813460 XP002103719 & SU 988 803 A (AS AZERB THEOR CHEM) , 15 January 1983 see abstract --- 	
A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 239 (C-367), 19 August 1986 & JP 61 072727 A (NIPPON SHEET GLASS CO LTD), 14 April 1986 cited in the application see abstract --- -/--	

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
26 May 1999	07/06/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Van Geyt, J

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 176 801 A (KUREHA CHEMICAL IND CO LTD) 7 January 1987 cited in the application -----	

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 2176801	A	07-01-1987	JP 61293936 A	24-12-1986
			DE 3620512 A	02-01-1987
			FR 2585016 A	23-01-1987